To: Hedrick, Elizabeth[Hedrick.Elizabeth@epa.gov]

From: Allgeier, Steve

**Sent:** Tue 1/14/2014 1:10:08 PM

Subject: FW: Odor Threshold ..... at least something ----- FW: Eastman Crude MCHM - 4-

methylcyclohexanemethanol

FYI – information about odor thresholds and the odorant.

From: Kelly, Jack (R3 Phila.)

Sent: Tuesday, January 14, 2014 7:57 AM

To: binetti, victoria; Wisniewski, Patti-Kay; Allgeier, Steve; Caporale, Cynthia; Burns, Francis; Matlock, Dennis;

Linden, melissa; Casillas, Laura; Ventura, Dominic Cc: Campagna, Philip; Newhart, Gary; Mickunas, Dave

Subject: Odor Threshold ..... at least something ----- FW: Eastman Crude MCHM - 4-methylcyclohexanemethanol

Jack Kelly

On Scene Coordinator

EPA Region III, Philadelphia

215-514-6792 (cell)

215-814-3112 (office)

From: Markiewicz, Karl

Sent: Tuesday, January 14, 2014 7:41 AM

To: loc3@cdc.gov

Cc: Werner, Lora; Kelly, Jack (R3 Phila.)

Subject: Fw: Eastman Crude MCHM - 4-methylcyclohexanemethanol

Hello Larry,

I tried sending this multiple times yesterday (sorry if rec'd already) but BB having some issues.

Obviously not the most rigorous odor threshold evaluation but its gets us in the ballpark.

Karl

From:	Γ	Ex. 4 - CBI	
	~		•

Sent: Monday, January 13, 2014 4:11:37 PM

To: Markiewicz, Karl

**Subject:** RE: Eastman Crude MCHM - 4-methylcyclohexanemethanol

That sounds like a good starting point Karl. About half the test subjects (n=15) responded that they couldn't smell, or weren't sure if they were smelling something at that level. They were then presented a 1 ppm sample and all subjects reported they could smell it. My Lab Techs have reported about the same experience. Samples analyzed at 0.1 ppm or less are essentially odor free. [Es. 6-Perconal Privacy absent mindedly did a taste test at 0.4 ppm taking some medication this morning. [Insert Privacy absent mindedly did a lingering solvent taste.]

Ex. 4 - CBI

Sr. Chemist

Dupont Chemicals and Fluoroproducts

Dupont Belle Plant

901 W Dupont Ave.

Belle, WV 25015

**Ex. 4 - CBI** 

From: Markiewicz, Karl [mailto:Markiewicz.Karl@epa.gov] Sent: Monday, January 13, 2014 12:49 PM
To: Ex. 4-CBI Subject: RE: Eastman Crude MCHM - 4-methylcyclohexanemethanol
Hello [Ex. 4-CBI]
I think I see light at the end of the tunnel – hopefully not a train.
I just spoke with <b>Ex. 4 - CBI</b> (Eastman) and he thought you'd developed a provisional odor threshold for mixture of 0.1 ppm. I assume it's for the licorice odor.
threshold for mixture of 0.1 ppm. I assume it's for the neoffice odor.
We're anticipating that when "all clear" is given people might sense an odor and have questions.
We'd like to be able to develop a message in anticipation of that event. Something like "Based on observational reports, the data suggests that odors might be detected at concentrations of
Crude MCHM at approximately 0.1 ppm (100 ppb). This provisional odor threshold is below the health-based screening number of 1.0 ppm."
Sincerely,
Karl
Karl V. Markiewicz PhD Senior Toxicologist

DHHS/CDC/ATSDR

MailStop: 3HS00

1650 Arch Street					
Philadelphia, PA 19103					
215-814-3149 (office)					
kvm4@cdc.gov					
From:   Ex. 4 - CB  Sent: Sunday, January 12, 2014 9:55 AM					
Sent: Sunday, January 12, 2014 9:55 AM To: Markiewicz, Karl					
Subject: RE: Eastman Crude MCHM - 4-methylcyclohexanemethanol					
No problem.					
From: Markiewicz, Karl [mailto:Markiewicz.Karl@epa.gov] Sent: Sunday, January 12, 2014 9:53 AM					
To: Ex.4-CBI					
Subject: Re: Eastman Crude MCHM - 4-methylcyclohexanemethanol					
Thanks Ex. 4-CBI					
Thanks (Ex. 4-cal)					
Is it OK to share your email with an EPA ERT chemist (Dave M) who is working on air issues					
associated with this release. We're all anticipating "air" questions and Dave is one of the air experts with ERT.					
experts with ERT.					
Sincerely,					
Karl					
From: Ex. 4 - CBI Sent: Sunday, January 12, 2014 9:44:42 AM					
From: [ Ex. 4 - CBl ] Sent: Sunday, January 12, 2014 9:44:42 AM					
To: Markiewicz, Karl					
Subject: RE: Eastman Crude MCHM - 4-methylcyclohexanemethanol					

Freedom\_0006690\_0004

Hi Karl,

I haven't had time to do an official MDL study, but component peaks have about a 2:1 s/n at the 0.01 ppm level, and matrix spikes and duplicates all look real good. To give ourselves a little leeway however, I have set our reporting limit as 0.1 ppm.

Levels in the feed to the water company plant are down at that level. The water exiting the plant is still between 0.5 and 1 ppm. It's hard to explain to some folks how activated carbon equilibria works. We're getting there.

Ex. 4 - CBI

From: Markiewicz, Karl [mailto:Markiewicz.Karl@epa.gov]

Sent: Sunday, January 12, 2014 7:08 AM

To: Ex. 4 - CBI

Cc: 1kw9@cdc.gov

Subject: Re: Eastman Crude MCHM - 4-methylcyclohexanemethanol

Thabks I Ex. 4 - CBI

Not problem - I know how hectic these responses are. I've seen emails indicating that the DL for MCHM is 10 ppb.

You guys are doing a great job and we appreciate all the support and effort.

Sincerely,

Karl

From: Ex. 4 - CBI

Sent: Sunday, January 12, 2014 3:31:01 AM

To: Markiewicz, Karl Cc: <a href="mailto:lkw9@cdc.gov">lkw9@cdc.gov</a>

Subject: RE: Eastman Crude MCHM - 4-methylcyclohexanemethanol

Hello Karl,

I started this reply once before and got pulled away. At this point I have had little time for anything other than monitoring of the primary component 4-methylcyclohexanemethanol. Besides setting up additional GC's in my lab, preparing standards for contract lab evaluation, preparing odor profile standards for multiple groups, and trying to keep up with the ever increasing sample load, I have also been assisting three National Guard Mobile units in setting up the analysis on their equipment (with limited success).

Some air monitoring samples on activated charcoal would have been nice to look at. Reports coming to me as my lab techs rotate in and out, are that recent rains have almost completely eliminated the odor downtown. A lost opportunity to study some dispersion patterns???

**Ex. 4 - CBI** (another chemist at the site) and I have had much the same suspicion as to the various odors.

Maybe once the dust settles I can go back and rehash the data.

**Ex. 4 - CBI** 

Sr. Chemist

Dupont Chemicals and Fluoroproducts

Dupont Belle Plant

901 W Dupont Ave.

Belle, WV 25015

**Ex. 4 - CBI** 

From: Markiewicz, Karl [mailto:Markiewicz,Karl@epa.gov]

Sent: Friday, January 10, 2014 2:42 PM

To: Ex. 4 - CBI

Cc: lkw9@cdc.gov

**Subject:** Eastman Crude MCHM - 4-methylcyclohexanemethanol

Hello Ex. 4 - CBI

I'm a toxicologist with CDC/ATSDR and involved with the WV spill response. I was given your email from a member of the response team within EPA.

I understand that you've developed the analytical standard and methods for 4-methylcyclohexanemethanol and maybe for all the components of the mixture. Can you provide detection limits for 4-methylcyclohexanemethanol and others if available?

We believe the licorice odor is related to the 4-(MethoxyMethyl) cyclohexaneMethanol (98955-27-2) in the mixture. Its my understanding that as time has progressed the licorice odor has diminished and a sweet (alcohol?) odor is now detectable. Do you think the ether has dissipated and now the alcohols are predominated the odor profile?

## Eastman Crude MCHM

Weight %	Component	CAS Registry No.
68 . 89%	4-methylcyclohexanemethanol	34885-03-5
4-22%	4-(methoxymethyl)cyclohexanemethanol	98955-27-2
4-10%	water	7732-18-5
5%	methyl4-methylcyclohexanecarboxylate	51181-40-9
1%	dimethyl 1,4-cyclohexanedicarboxylate	94-60-0
1%	methanol	67-56-1
1-2%	1,4-cyclohexanedimethanol	105-08-8

Sincerely,

Karl

Karl V. Markiewicz PhD

Senior Toxicologist DHHS/CDC/ATSDR

MailStop: 3HS00

1650 Arch Street

Philadelphia, PA 19103

215-814-3149 (office)

kvm4@cdc.gov

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